Innovative Characterization of Amorphous and Thin-Film Silicon for Improved Module Performance

Research results during the first quarter of Phase III of NREL Subcontract XXL-5-44205-09 are reported. During this quarter we have continued collaborations with United Solar Ovonics Corporation on defects that contribute to the Staebler-Wronski effect in modules made using a-Si:H intrinsic layers. Specifically, we have continued NMR measurements on another set of device-quality samples on which we have employed pulsed annealing to increase the defect densities. In addition, we are continuing our studies of light soaking at 77 K on two different samples to compare with the case of the tritium decay in the tritiated samples. In this quarter we report on collaborative studies with the group of Howard Branz (Pauls Stradins, Yueqin Xu, Falah Hasoon and Qi Wang) and with Professor Walter Harrison at Stanford. The idea is to get information on hydrogen motion by evolving hydrogen out of the sample in sequential steps. In addition, solid-phase crystallization and the subsequent re-hydrogenation of the amorphous silicon thin films provides a low cost approach for thin-film crystalline Si:H-based photovoltaic devices [1,2]. During the hydrogen effusion, significant lattice reconstruction occurs, as hydrogen is driven out of the film. This process is accompanied by creation and migration of a large number of dangling bonds. Optical techniques, such as measurements of the reflectance and transmittance, provide *in situ* information of the kinetics of the crystallization [1,2]. However, these techniques do not provide information of local structural changes during crystallization. Experimentally, samples prepared by HWCVD crystallize faster and at lower temperatures, compared to samples made by PECVD [1,2]. This phenomenon is not well understood. In addition, although most of the hydrogen is driven out of the film, there exists a rather persistent residual hydrogen concentration of about 10^{19} cm^{-3}. It is not clear if this residual hydrogen plays any role during the crystallization. Another is the effect of re-hydrogenation after the film is crystallized. The local order of the hydrogen atoms is crucial in understanding the effect of hydrogen passivation of the excessive defects.

We have investigated the evolution of the defects created during hydrogen effusion and the crystallization process, using magnetic resonance techniques such as nuclear magnetic resonance (NMR) and electron spin resonance (ESR). In this quarterly status report, we show the results from ESR during the annealing and crystallization and present a simple model of the exchange interaction in the disordered a-Si.

Amorphous silicon samples were deposited by both HWCVD and PECVD at the facility at National Renewable Energy Laboratory (NREL). Information of the samples is listed in Table I. One HWCVD sample (H2029) and one PECVD sample (L1477) were annealed at the same time at $T = 560°C$ in nitrogen gas. A second PECVD sample was annealed at $T = 580°C$ for 1300 min, and reflectance measurements show that the film crystallized after $t \sim 1050$ min. The annealing is monitored by a n&k reflectance and transmittance spectrometer.

Table I. Growth conditions of the HWCVD and PECVD *a*-Si:H samples.

Sample #	Deposition method	Substrate temperature (°C)	Deposition rate (Å/s)	Thickness (μm)
L1447	PECVD	250	1-2	~1
H2029	HWCVD	400	7	~1

ESR measurements of the defect densities were carried out on a Bruker Elex 500 Spectrometer at room temperature. The defect densities were obtained by comparing the double integrated intensity in the samples to that in a standard weak pitch sample measured under the same conditions.

Figure 1 shows the evolution of the defect densities in H2029 and L1477 as a function of the annealing time at $T = 560 °C$. In the HWCVD sample (H2029), the defect density begins to decrease after about 60 min, and the film is fully crystallized after about 750 min. Reflectance measurements show that crystallization occurs during the same time period. After the film is crystallized, the defect density deceases to about 4×10^{17} cm^{-3} and remains at this value through the rest of the annealing.

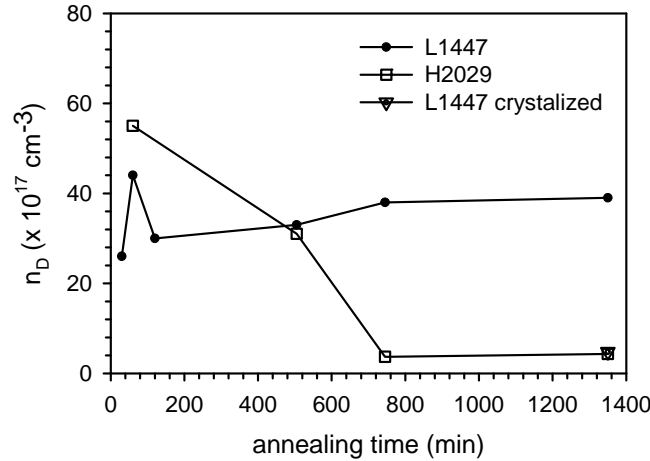**Figure 1** The defect densities in HWCVD (H2029) and PECVD (L4774) samples as a function of annealing time at $T = 560 °C$. Open squares and solid circles indicate data for HWCVD and PECVD samples, respectively. The open triangle indicates defect the density of the PECVD sample after annealing at $T = 580 °C$ for *t*~1300 min.

The defect density in PECVD sample (L4774) shows an initial sharp increase to about 4×10^{18} cm^{-3}, followed by a decease to 3×10^{18} cm^{-3}, and a gradual increase over the remainder of the annealing. This sample does not show any evidence of crystallization, which is consistent with the reflectance measurements. Due to the lack of detailed data on the HWCVD sample, we will focus our discussion in the PECVD sample.

Figure 2 shows the comparison of the lineshapes of the ESR signals in H-effused and crystallized samples to that in a typical *a*-Si:H sample. In trace (a), which is from a typical *a*-

Si:H sample, the peak-to-peak width is about 7 G. Trace (b) is from the sample in the H-effused state before crystallization, the line-width is about 5 G. The line-width of the crystallized sample (6.5 G) is much smaller than previously reported values in micro-crystalline silicon (μc-Si:H) samples [3]. The lineshape changes can be attributed to exchange-narrowing that is well known for high defect density films [4]. This narrowing effect will be discussed in detail later. Figure 2 also shows a slight difference in the g-values as calculated from the field of zero crossing, which could be due to the difference in ESR resonance frequency or to a slight change in *g*-value of the defect signal.
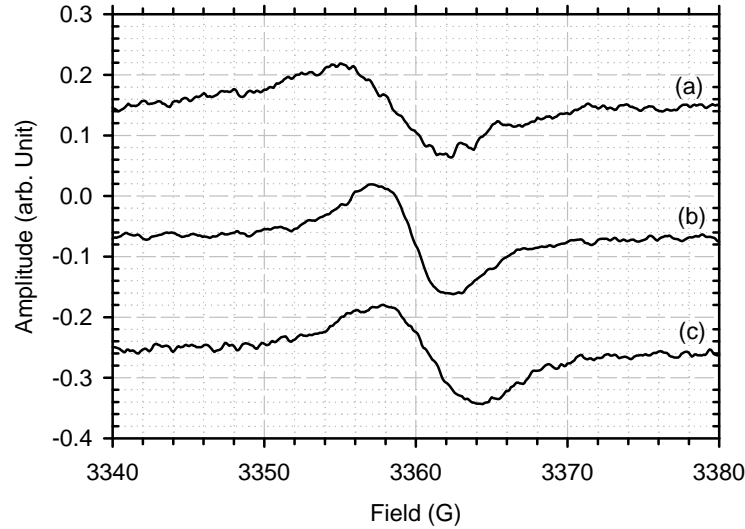

Figure 2. Comparison of the ESR lineshapes in H-effused and crystallized samples to a typical *a*-Si:H sample. (a) typical a-Si:H, (b) H-effused, before crystallization ($n_D = 3.6 \times 10^{18}$ cm^{-3}), and (c) after crystallization ($n_D = 4.3 \times 10^{17}$ cm^{-3}). The amplitudes are scaled to show the difference in line-width.

Since only the total number of spins is measured in typical ESR spin count measurements, these measurements do not determine whether or not the spins are clustered. The bulk defect density is only accurate based on the assumption that the defects are randomly distributed within the sample. This is unlikely during the crystallization, as well as right before and after crystallization. To investigate the potential clustering of the spins, we compared the lineshape in the hydrogen effused PECVD sample to that in an a-Si:HT sample. In a-Si:HT, the defects are crested by decay of the tritium toms that are bonded to silicon atoms,

$$^3H \longrightarrow {}^3He + ß^- + \text{anti-neutrino} + 5.7 \text{ keV} \qquad (1)$$
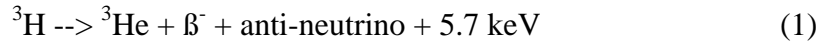
The resulting ^{3}He atom will detach from the silicon atom and leave a dangling bond on the Si atom. The energy of the β particle is ~ 5.7 keV. Irradiating the sample with an electron beam with the same energy and dosage shows that no significant amount of defects are created [5, 6]. Therefore the main mechanism for defect creation is due to the reaction in Eq. (1). This process does not involve large-scale lattice reconstruction, due to the slow decay rate of the tritium nuclei, and therefore this process presumably creates defects that are more likely to be

randomly distributed. Figure 3 shows the dependence of the line-width on the defect densities in one a-Si:HT sample. For comparison, the line-width of the H-effused PECVD sample with a bulk defect density of $n_D = 3.6 \times 10^{18}$ cm^{-3} and the line-width in an a-Si sample prepared by RF sputtering [4] are also shown.
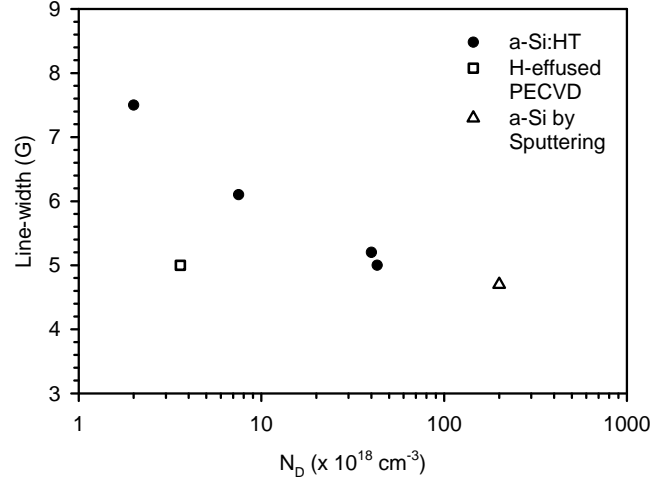

Figure 3   The dependence of the ESR line-width on the defect densities in a-Si:HT sample and in H-effused a-Si:H sample prepared by PECVD. Solid circles represent the data from the a-Si:HT sample, the open square represents the line-width for the defect density of $n_D = 3.6 \times 10^{18}$ cm^{-3} in the H-effused PECVD sample. The open triangle is the line-width from Ref. [4] in a-Si sample prepared by RF sputtering.

Figure 3 clearly shows the discrepancy in line-width between the H-effused PECVD sample and the a-Si:HT sample with the same bulk defect density. The defect density in a-Si:HT is about one order of magnitude higher with the same line-width (~5 G). If we assume the defects are randomly distributed in a-Si:HT, then there must be significant clustering in the H-effused sample to have a comparable line-width, with a much lower bulk defect density. This result will be further discussed below.

It is well known that at high spin densities, the observed ESR line-width is narrower due to the so-called exchange-narrowing effect [7]. This effect arises from the exchange interaction between the spins, and has the form

$$H_{ex} = J\vec{S}_1 \cdot \vec{S}_2 \, , \tag{2}$$

where $\vec{S}_1$ and $\vec{S}_2$ are the spins of the two defects. J is the coupling constant. This interaction allows the spin-pair to undergo rapid mutual flipping and effectively average out the broadening due to other interactions, such as the dipole-dipole interaction between the spins and g-tensor anisotropy. The exchange interaction deceases rapidly as the distance between the two spins increases, and therefore this interaction does not affect the line-width at low spin densities. Although this effect has been extensively studied in crystalline materials, no details to estimate the coupling constant have been reported. Here we develop a rather simple method to estimate the interaction in a-Si:H.

Consider two defects (dangling bonds) that are separated by n Si atoms. In this case, the exchange-interaction will be through the n-1 bonds in between. The dangling bond, which is a singly occupied sp^3 hybrid on a Si atom, interacts with another dangling bond by coupling to the Si-Si bond on the same atom, which in turn couples to another Si-Si bond, and so on. If we only consider the coupling through the bonding orbitals, the matrix of the total Hamiltonian is an $(n+1)\times(n+1)$ matrix,

$$
\begin{pmatrix}
0 & \frac{V_1}{\sqrt{2}} & 0 & \cdot & \cdot & \cdot & 0 \\
\frac{V_1}{\sqrt{2}} & -V_2 & \frac{V_1}{2} & \cdot & & & \cdot \\
0 & \frac{V_1}{2} & \cdot & \cdot & \cdot & & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot\cdot \\
\cdot & & \cdot & \cdot & \cdot & \frac{V_1}{2} & 0 \\
\cdot & & & 0 & \frac{V_1}{2} & -V_2 & \frac{V_1}{\sqrt{2}} \\
0 & \cdot & \cdot & \cdot & 0 & \frac{V_1}{\sqrt{2}} & 0
\end{pmatrix}
\tag{3}
$$

where $\dfrac{V_1}{\sqrt{2}}$ is the coupling between the dangling bond and the Si-Si bond, $\dfrac{V_1}{2}$ is the coupling between two hybrids within a bond, and V_2 is the energy gained by forming the bonding orbital. Diagonalization of this matrix results in $n+1$ energy levels, of which n-1 levels are close to V_2 (bonding orbitals). The other two energy levels are higher and are separated only by a small energy, which is due to the exchange interaction between the two dangling bonds.

To estimate the onset of the exchange-narrowing of the lineshape, we assume that the narrowing will be measurable when the exchange interaction is about the same as the line-width of the ESR signal. By choosing $V_1 = 1.8$ eV and $V_2 = 4.4$ eV for Si [8], we numerically diagonalized the Hamiltonian (Eq. 3), and obtained a value of the exchange interaction of $\Delta E_{ex} = 5.4\times10^{-8}$ eV when the two dangling bonds are separated by 12 atoms. This value of ΔE_{ex} corresponds to an ESR line-width of about 4.6 G. The defect density is calculated to be about 3×10^{19} cm^{-3}, with an average distance between two defects of 12 inter-atomic distances of Si. This is consistent with the experimentally observed relation between defect density and the ESR line-width in a-Si:HT, in which we assume the defects are randomly distributed, and not significant clustered.

We found that ΔE_{ex} decreases exponentially with an increasing number of bonds between the two dangling bonds. Therefore, the exchange interaction is effectively a short-range interaction. As a consequence, our results do not distinguish between the case in which more than two defects are close to each other and the case in which only paired defects are present.

In summary, we have performed ESR measurements in H-effused a-Si:H thin films made by both HWCVD and PECVD. The evolution of the defect density as a function of annealing time is consistent with that found in optical measurements. Analysis of the line-width shows that

in H-effused states, the defects are either clustered or exist in pairs. A simple model of the exchange interaction in *a*-Si can account for the difference in line shapes observed in these films as compared to *a*-Si:HT samples described in a previous status report.

In addition to our studies on hydrogen doublets with United Solar Ovonics, we are continuing our collaborative studies on tritiated samples with NREL. Also, we are continuing our irradiation of device quality samples of a-Si:H at 77 K for long periods of time to test for saturation.

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